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(71) Applicant (for all designated States except US):
PENNZOIL-QUAKER STATE COMPANY [US/US];
700 Milam, P.O. Box 2967, Houston, TX 77002 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): CHIU, I-Ching
[US/US]; 9707 W. Airport Blvd., Houston, TX 77031
(US). GUNSEL, Selda [US/US]; 135 Green Gables Cir.,
The Woodlands, TX 77382 (US). LACEY, Paul [GB/US];
15 Summer Morning Ct., The Woodlands, TX 77381 (US).

(74) Agent: BAI, Benjamin, J.; Jenkins & Gilchrist, Suite
1800, 1100 Louisiana, Houston, TX 77002 (US).

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(54) Title: ENVIRONMENTALLY FRIENDLY LUBRICANTS

(57) Abstract: A biodegradable lubricant that is at least 60% biodegradable and has a gelation index of about 12 or less can be formulated using a transesterified triglyceride base oil together with a synthetic ester. A combination of an ester viscosity index improver and an olefin copolymer viscosity index improver also can be added. Further, the composition can be blended with mineral oils to lower the polarity in order to employ standard dispersant/inhibitor packages. Further, by mixing high and low viscosities of mineral oil in the formulation, it is possible to prepare a full range of SAE grade engine oils for gasoline-fueled and diesel-fueled engines.

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ENVIRONMENTALLY FRIENDLY LUBRICANTS**FIELD OF THE INVENTION**

This invention relates to environmentally friendly engine lubricant compositions suitable for internal combustion engines, and in particular for use in gasoline-fueled and
5 diesel-fueled engines.

BACKGROUND OF THE INVENTION

Vegetable oil triglycerides are available for use in food products and cooking. Many such vegetable oils contain natural antioxidants such as phospholipids and sterols that prevent oxidation during storage. Triglycerides are considered the esterification
10 product of glycerol with three molecules of carboxylic acids. The amount of unsaturation in the carboxylic acid affects the susceptibility of the triglyceride to oxidize. Oxidation can include reactions that link two or more triglycerides together through reactions of atoms near the unsaturation. These reactions may form higher molecular weight material which can become insoluble and discolored e.g. sludge. Oxidation can also result in
15 cleavage of the ester linkage or other internal cleavage of the triglycerides. The fragments of the triglyceride from the cleavage, being lower in molecular weight, are more volatile. Carboxylic acid groups generated from the oxidation of triglyceride make the lubricant acidic. Aldehyde groups may also be generated. Carboxylic acid groups have attraction for oxidized metals and can solubilize them in oil promoting metal
20 removal from some surfaces of lubricated metal parts.

Due to oxidation problems with natural triglycerides, most commercial lubricants are formulated from petroleum distillates which have lower amounts of unsaturation making them resistant to oxidation. Petroleum distillates require additives to reduce wear and oxidation, lower the pour point and modify the viscosity index (to adjust either the
25 high or low temperature viscosity) etc. The petroleum distillates are resistant to biodegradation and the additives used to adjust certain characteristics (often containing metals and reactive compounds) further detract from the biodegradability of the spent lubricant.

Synthetic ester lubricants having little or no unsaturation in the carbon to carbon
30 bonds are used in premium quality motor oils due to their desirable properties. However the acids and alcohols used to make synthetic esters usually are derived from petroleum distillates and are thus not from a renewable source. Synthetic lubricants are also more costly and less biodegradable than natural triglycerides.

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The finite supply of petroleum coupled with concern over the environmental effects from spills and disposal of petroleum based lubricants has fueled interest in the use of vegetable oils as viable substitutes for lubricants. Vegetable oils have the advantages of having a high flash point and excellent lubricating properties, while also being biodegradable and renewable. However, vegetable oils also have relatively poor flow characteristics at low temperatures and relatively poor oxidative stability which prevent their uses in some of the more extreme environments.

The vast majority of efforts to produce vegetable oil lubricants have utilized oils high in natural oleic acid levels, such as safflower, sunflower, corn, soybean and rapeseed oils. These polyunsaturated oils have lower oxidative stability, whereas fully saturated oils tend to crystallize at low temperatures. Thus, the use of oils with a high preponderance of the monounsaturated fat, oleic acid, provides a reasonable compromise between these two extremes.

In order to provide engine lubricants based on vegetable oils, certain standards should be met, including specifications required by SAE (Society of Automotive Engineers), API (American Petroleum Institute) and ILSAC (International Lubricant Standardization and Approval Committee). In particular, the SAE low temperature viscosity requirements have been difficult to meet in vegetable based oils. Further, an oil for use in internal combustion engines should also satisfy the most current requirements of the GF-3/API SL minimum performance standards, including a gelation index of less than about 12; high temperature TEOST (thermo-oxidative engine oil simulation) of total deposits of 45 mg maximum; remain homogeneous and miscible when mixed with SAE reference mineral oils; low volatility; phosphorous level of 0.1% maximum; and has to pass foam, filterability and ball rust test.

Therefore, there is a need for a vegetable oil-based lubricant that can be used as internal combustion engine oils of varying SAE viscosities that meet the current GF-3/API SL specifications and are at least about 60% biodegradable.

SUMMARY OF THE INVENTION

The above need is met by various embodiments of the invention. In some embodiments, an environmentally friendly lubricant comprises a transesterified triglyceride oil and a synthetic ester different from the triglyceride oil, the lubricant having a gelation index less than about 12 and being at least 60% biodegradable. The lubricant can be used as an automobile engine oil and may further include viscosity

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index improvers and/or detergent inhibitor (DI) packages. The automobile engine oil may also include other additives, such as a pour point depressant, antioxidant, friction modifier, rust inhibitor, corrosion inhibitor and anti-foaming agent. Additional embodiments are explained in the following description.

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BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph of gelation index (Gi) against the weight percent of viscosity modifier (VII) for various lubricants made in embodiments of the invention.

DESCRIPTION OF EMBODIMENTS OF THE INVENTION

Embodiments of the invention provide an environmentally friendly lubricant for use under a variety of operating conditions in automobiles, trucks, vans, buses, and off-highway farm, industrial, and construction equipment. Preferably, the oil is at least about 60% biodegradable according to ASTM D5864-95 and meets one or more of the current standards according to the Society of Automotive Engineers (SAE), American Petroleum Institute (API) and the International Lubricant Standardization and Approval Committee (ILSAC), which are incorporated by reference herein in their entirety.

In the following description, all numbers disclosed herein are approximate values, regardless whether the word "about" or "approximate" is used in connection therewith. They may vary by 1 percent, 2 percent, 5 percent, or, sometimes, 10 to 20 percent. Whenever a numerical range with a lower limit, R^L and an upper limit, R^U , is disclosed, any number falling within the range is specifically disclosed. In particular, the following numbers within the range are specifically disclosed: $R = R^L + k \cdot (R^U - R^L)$, wherein k is a variable ranging from 1 percent to 100 percent with a 1 percent increment, i.e., k is 1 percent, 2 percent, 3 percent, 4 percent, 5 percent, ..., 50 percent, 51 percent, 52 percent, ..., 95 percent, 96 percent, 97 percent, 98 percent, 99 percent, or 100 percent. Moreover, any numerical range defined by two R numbers as defined in the above is also specifically disclosed.

The following are test properties, definitions and test methods used in the description and examples that follow:

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Table 1: Testing Methods and Terminology

Properties	Test Method
Biodegradability	ASTM D5864
Scanning Brookfield Viscosity	ASTM D5133
Cold Cranking Simulator (CCS)	ASTM D5293
Gelation Index	ASTM D5133-99
Gelation Temperature	ASTM D5133-99
Kinematic Viscosity	ASTM D445
Determination of Yield Stress and Apparent Viscosity of Engine Oils at Low Temperature (MRV TP-1)	ASTM D4684-98
Pour Point	ASTM D97
Viscosity at High Shear Rate and High Temperature by Tapered Bearing Simulator (TBS)	ASTM D4683
Viscosity Index	ASTM D2270
Viscosity	ASTM D445
Volatility at 371°C (Simulated Distillation, Flash Point)	ASTM 6417
Evaporation % Wt. Loss (NOACK)	ASTM D972

Definitions

ASTM stands for American Society for Testing and Materials which provides standard protocols for material evaluation.

- 5 Biodegradability is a measure of a lubricants biodegradability. ASTM D 5864 determines lubricant biodegradation. The test determines the rate and extent of aerobic aquatic biodegradation of lubricants when exposed to an inoculum under laboratory conditions. The degree of biodegradability is measured by calculating the rate of conversion of the lubricant to CO₂. A lubricant is classified as readily biodegradable
- 10 when 60 percent or more of the test material carbon is converted to CO₂ in 28 days, as determined using this test method. In some embodiments, the lubricants have a biodegradability of at least 65%, 70%, 75%, 80%, 85%, 90%, or 95%.

- BROOKFIELD VISCOSITY is viscosity, in centipoises, as determined on the Brookfield viscometer. The operating principle for the Brookfield viscometer is the
- 15 torque resistance on a spindle rotating in the fluid being tested. Although Brookfield viscosities are most frequently associated with low temperature properties of gear oils and transmission fluids, they are in fact determined for many other types of lubricants.

- COLD Cranking STIMULATOR (CCS) is an intermediate shear rate viscometer and measures the resistance of an oil to engine cranking at low temperatures. CCS is
- 20 controlled largely by the additives in the oil and the viscosity index of the base oil.

GELATION INDEX is defined as the largest rate of change of viscosity increase when slowly cooled from -5°C to the lowest test temperature. The gelation index is a

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number indicating the oil's tendency to form a gelled structure in the oil at colder temperatures. Numbers above 6 indicate some gelation-forming tendencies. Numbers above 12 are of concern to engine makers. Numbers above 15 have been associated with field-failing oils. Gelation index is determined in accordance with ASTM D-5133, which is incorporated by reference herein in its entirety. The gelation index can be measured by the Scanning Brookfield Technique in accordance with ASTM D5133. In this test, a tube of oil containing a rotor driven at 0.3 RPM is slowly cooled at 1 °C per hour for approximately two days, typically from -5 °C (23 °F) to -45 °C (-40 °F). As the sample is cooled, the viscosity is measured by the increasing torque generated by a spindle rotating in the oil at constant speed. A plot of the overall viscosity curve is generated. The gelation index is determined accordingly.

GELATION POINT also known as GELATION TEMPERATURE is defined as the temperature at which the gelation index occurs. Gelation temperature is determined in accordance with ASTM D-5133, which is incorporated by reference herein in its entirety.

KINEMATIC VISCOSITY (KV) is viscosity now commonly reported in centistokes (cSt), measured at either 40°C or 100°C.

YIELD STRESS AND Apparent LOW TEMPERATURE VISCOSITY (MRV YS and MRV TP-1) measures the borderline pumping temperature for engine oils. An engine oil is held at 80°C in a mini-rotary viscometer and slowly cooled at a programmed cooling rate to a final test temperature, a low torque is applied to the rotor shaft to measure yield stress, then a higher torque is applied to determine the apparent viscosity of the sample.

POISE is the CGS unit of absolute viscosity. This is the shear stress (in dynes per square centimeter) required to move one layer of fluid along another over a total layer thickness of one centimeter at a shear rate of one centimeter per second. Dimensions are dyne-sec/cm². The centipoise (cP) is 1/100 of a poise and is the unit of absolute viscosity most commonly used. Whereas ordinary viscosity measurements depend on the force of gravity on the fluid to supply the shear stress and are thus subject to distortion by differences in fluid density, absolute viscosity measurements are independent of density and are directly related to resistance to flow.

POUR POINT is a widely used low-temperature flow indicator defined as the lowest temperature at which an oil or distillate fuel is observed to flow when cooled

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under conditions prescribed by test method ASTM D97. The pour point is 3°C (5°F) above the temperature at which the oil in a test vessel shows no movement when the container is held horizontally for five seconds.

TAPERED Bearing SIMULATOR (TBS) measures high temperature high shear rate viscosity of motor oils, very high shear rates are obtained by using an extremely small gap between the rotor and stator wall.

VISCOSITY index (VI) measures the rate of change of viscosity with temperature, determined by formula from the viscosities at 40°C and 100°C in accordance with ASTM D567 (or D2270 for VI's above 100).

VISCOSITY is a measure of a fluid's resistance to flow. It is ordinarily expressed in terms of the time required for a standard quantity of the fluid at a certain temperature to flow through a standard orifice. The higher the value, the more viscous the fluid. Since, viscosity varies inversely with temperature, its value is meaningless unless accompanied by the temperature at which it is determined. With petroleum oils, viscosity is now commonly reported in Centistokes (cSt), measured at either 40°C or 100°C (ASTM Method D445 - Kinematic Viscosity).

VOLATILITY is a property of a liquid that defines its evaporation characteristics. Of two liquids, the more volatile boils at a lower temperature, and it evaporates faster when both liquids are at the same temperature. The volatility of petroleum products can be evaluated by tests for Flash Point, Simulation Distillation and volatility weight loss (NOACK).

Generally, the environmentally friendly lubricant in accordance with embodiments of the invention is a mixture of transesterified vegetable oil and esters. The lubricant has a gelation index of less than about 12. In some embodiments, the gelation index is less than about 10, less than about 8, less than about 6, less than about 4, or less than about 2. Preferably, the lubricant meets one or more of the current standards of the Society of Automotive Engineers (SAE), American Petroleum Institute (API) and the International Lubricant Standardization and Approval Committee (ILSAC) and is at least about 60% biodegradable according to the ASTM D 5864 test which defines the lubricant as readily biodegradable. Various types of vegetable oils may be present in the lubricant. For example, the transesterified vegetable oil may be a mixture of transesterified corn, rapeseed, soybean, and sunflower oil. The transesterified vegetable oil is mixed with esters that lower the gelation index and improve viscosity.

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Table 2 indicates various compositions of environmentally friendly lubricant compositions in accordance with embodiments of the invention.

Table 2

Component	Preferred Range (wt.%)	More Preferred Range (wt.%)	Most Preferred Range (wt.%)	Possible Range (wt.%)
Transesterified Triglyceride	30 - 85	35 - 75	40 - 65	0.5 - 99.5
Synthetic Ester	10 - 30	12 - 25	15 - 20	0.5 - 99.5
Ester Type Viscosity Index Improver	0 - 3	0.2 - 2.5	0.5 - 2	0.5 - 99.5
Olefin Copolymer Type Viscosity Index Improver	0 - 6	1 - 5	2 - 4	0.5 - 99.5
Dispersant/Inhibitor Package	8 - 16	10 - 12	5 - 10	0.5 - 99.5
Additives	0 - 5	0 - 2	1 - 2	0.5 - 99.5
Mineral Oil	0 - 40	5 - 30	10 - 25	0.5 - 99.5

In some embodiments, the environmentally friendly lubricant is a mixture of a

5 transesterified vegetable oil in an amount from about 30 to about 85%, more preferably from about 35 to about 75%, and most preferred from about 40 to about 65%; a synthetic ester in an amount from about 10 to about 30%, more preferred from about 12 to about 25%, and most preferred from about 15 to about 20%. Optionally, an ester type viscosity index improver may be added in an amount from about 0.1 to about 3.0%, more

10 preferred from about 0.2 to about 2.5%, most preferred from about 0.5 to about 2%; further, an olefin copolymer type viscosity index improver is optionally added in an amount from about 0.1 to about 6.0%, more preferred from about 1 to about 5%, most preferred from about 2 to about 4%. The environmental lubricant further optionally includes a dispersant/inhibitor package in an amount from about 8 to about 14%, more

15 preferred from about 10 to about 12%; and other additives, such as a pour point depressant, antioxidant, friction modifier, rust inhibitor, corrosion inhibitor, and anti-foaming agent, in the amount from about 0.1 to about 5%, more preferred from about 0 to about 2%. The environmentally friendly lubricant is formulated to have a gelation index of less than about 12 and is at least about 60% biodegradable in the ASTM D-

20 5864-95 biodegradability test. The environmentally friendly lubricant also meets all ILSAC GF-3/API SL bench tests.

In other embodiments, transesterified vegetable oils in the environmentally friendly lubricant are in the amount from about 30 to about 85 wt%, more preferably from about 35 to about 75 wt%, and most preferred from about 40 to about 65 wt%.

25 Suitable transesterified vegetable oils include, but are not limited to those described in

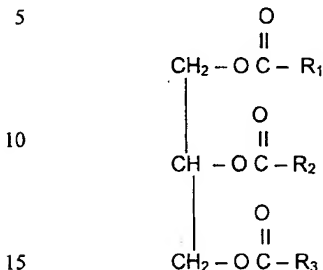
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the following U. S. Patents which are incorporated by reference herein in their entirety: 6,420,322; 6,414,223; 6,291,409; 6,281,375; 6,278,006; 6,271,185; and 5,885,643.

For example, one such transesterified vegetable oil comprises a glycerol polyol ester having the following formula, as disclosed in U. S. Patent No. 6,278,006:



wherein R₁, R₂, and R₃ are aliphatic hydrocarbyl groups having from about 4 to about 24 carbon atoms inclusive, wherein at least one of R₁, R₂, and R₃ have a saturated aliphatic hydrocarbyl moiety having about 4 to about 10 carbon atoms inclusive, and
 20 wherein at least one of R₁, R₂, and R₃ have an aliphatic hydrocarbyl moiety having from about 12 to about 24 carbon atoms inclusive. These triglycerides are available from a variety of plants or their seeds and are commonly referred to as vegetable oils. R₁, R₂ and R₃ may be different moieties or the same moiety.

Within the triglyceride formula are aliphatic hydrocarbyl groups having at least
 25 60 percent monounsaturated character and containing from about 6 to about 24 carbon atoms. The term "hydrocarbyl group" as used herein denotes a radical having a carbon atom directly attached to the remainder of the molecule. The aliphatic hydrocarbyl groups include the following:

(1) Aliphatic hydrocarbon groups; that is, alkyl groups such as heptyl, nonyl,
 30 undecyl, tridecyl, heptadecyl; alkenyl groups containing a single double bond such as heptenyl, nonenyl, undecenyl, tridecenyl, heptadecenyl, heneicosenyl; alkenyl groups containing 2 or 3 double bonds such as 8,11-heptadecadienyl and 8,11,14-heptadecatrienyl. All isomers of these are included, but straight chain groups are preferred.

35 (2) Substituted aliphatic hydrocarbon groups; that is groups containing non-hydrocarbon substituents which do not alter the predominantly hydrocarbon character of the group. Those skilled in the art will be aware of suitable substituents; examples are

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hydroxy, carbalkoxy (especially lower carbalkoxy), and alkoxy (especially lower alkoxy). The term, "lower" denoting groups containing not more than 7 carbon atoms.

(3) Hetero groups; that is, groups which, while having predominantly aliphatic hydrocarbon character contain atoms other than carbon present in a chain or ring otherwise composed of aliphatic carbon atoms. Suitable hetero atoms will be apparent to those skilled in the art and include, for example, oxygen, nitrogen and sulfur.

Naturally occurring triglycerides are vegetable oil triglycerides. Transesterified triglycerides may be formed by the reaction of one mole of glycerol with three moles of a fatty acid or mixture of fatty acids or by the chemical modification of a naturally occurring vegetable oil. Regardless of the source of the triglyceride oil, the fatty acid moieties are such that the triglyceride has a monounsaturated character of at least about 60 percent, preferably at least about 70 percent and most preferably at least about 80 percent. The transesterified triglyceride may also have a monounsaturated character of at least about 85, 90, or 95 %.

Preferred transesterified vegetable oils have relatively high oxidative stability and good low temperature viscosity properties. Oxidative stability is related to the degree of unsaturation in the oil and can be measured, e.g., with an Oxidative Stability Index instrument, Omnion, Inc., Rockland, Mass. according to AOCS Official Method Cd 12b-92 (revised 1993). Oxidative stability is often expressed in terms of "AOM" hours. For example, oxidative stability of oils can range from about 40 AOM hours to about 120 AOM hours or from about 80 AOM hours to about 120 AOM hours. The transesterified vegetable oils used in some embodiments have excellent low temperature viscosity properties. A higher viscosity index value indicates that the viscosity of the oil changes less with a change in temperature. In other words, the higher the viscosity index, the greater the resistance of the lubricant to thicken at low temperatures and thin out at high temperatures. Transesterified vegetable oils used in certain embodiments have a pour point from about 0 °C to about -30 °C. The vegetable oils are liquid at room temperature and have a melting point of about 6 °C or less.

The vegetable oils may be genetically modified such that they contain a higher than normal oleic acid content. High oleic vegetable oils contain at least about 60% oleic acid. These high oleic oils have lower oxidative stability, whereas fully saturated oils tend to crystallize at low temperatures. Normal sunflower oil has an oleic acid content of 25-30 percent. By genetically modifying the seeds of sunflowers, a sunflower

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oil can be obtained wherein the oleic acid content is from about 60 percent up to about 90 percent. U. S. Patents No. 4,627,192 and No. 4,743,402 are herein incorporated by reference for their disclosure to the preparation of high oleic sunflower oil and its method of measuring the oleic acid content.

- 5 High oleic vegetable oils can be high oleic safflower oil, high oleic corn oil, high oleic rapeseed oil, high oleic sunflower oil, high oleic soybean oil, high oleic cottonseed oil, high oleic lesquerella oil, high oleic meadowfoam oil and high oleic palm olein. A preferred oil is the AGRI-PURE 560™ which is a transesterified high oleic acid sunflower oil with short saturated fatty acid esters. AGRI-PURE 560™ is a synthetic
10 polyolester TAG base oil by CARGILL (Minneapolis, MN).

The specifications according to the manufacturer for AGRI-PURE 560™ are:

Table 3: AGRI-PURE 560™

Property	Agri-Pure 560	Test Method
Viscosity at 40°C	28.76 cSt	ASTM D445
Viscosity at 100°C	6.47 cSt	ASTM D445
Viscosity Index	189	ASTM D2270
Noack volatility	3.5 %	ASTM D6375-99A
Specific Gravity	0.924 g/ml	ASTM D1298
Density	7.39 lbs/gal	By conversion
Flash Point	247°C	ASTM D92
Oxidative Stability	>1500 hrs	ASTM D943 Dry
PDSC, 180°C	38 minutes	ASTM D6186-98
Biodegradability	>95 %	CEC L33-A-94
Biodegradability	>80 %	ASTM D5864-95

- Additional preferred TAG base oils include a high oleic sunflower oil available as SUNYL 80™ and a high oleic rapeseed oil available as RS-80™, both from SVO
15 ENTERPRISES (Eastlake, Ohio). Other high oleic oils include high oleic sunflower oils available from DOW, DUPONT, or Instituto de la Grasa, high oleic canola oils from CARGILL or DUPONT, high oleic soybean oils from DUPONT or MONSANTO, high oleic corn oils from DUPONT, and high oleic peanut oils from MYCOGEN or the University of Florida.

- 20 Non-genetically modified vegetable oils are sunflower oil, safflower oil, corn oil, soybean oil, rapeseed oil, meadowfoam oil, lesquerella oil, castor oil or olive oil. It is to be noted that olive oil is naturally high in oleic acid. The oleic acid content of olive oil typically ranges from about 65 to about 85 percent.

- 25 Any vegetable oil can be transesterified by the addition of a saturated ester, preferably a short chain fatty acid or a polyol ester. This addition results in random esterification of the short chain fatty acids to the glycerol backbone of the vegetable oil.

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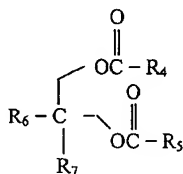
In general, transesterification can be performed by adding a short chain fatty acid ester to a vegetable oil in the presence of a suitable catalyst and heating the mixture. Esters of short chain fatty acids include methyl esters and polyol esters. Methyl esters can be produced, for example, by esterification of fatty acids.

5 Polyol esters also can be used in the transesterification of vegetable oils. As used herein, "polyol esters" refers to esters produced from polyols containing from two to about 10 carbon atoms and from two to six hydroxyl groups. Preferably, the polyols contain two to four hydroxyl moieties.

Transesterification of a polyol ester with a vegetable oil results in the short fatty acid chains of the polyol and the long fatty acid chains of the TAG being randomly distributed among both the polyol and glycerol backbones. In one embodiment, transesterified vegetable contain TAGs having a structure as defined above, and/or a non-glycerol polyol ester having the following structure:

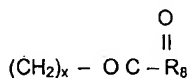
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wherein R_4 and R_5 are independently aliphatic hydrocarbyl groups having from about 4 to about 24 carbon atoms inclusive, wherein at least one of R_4 and R_5 have a saturated aliphatic hydrocarbyl moiety having about 4 to about 10 carbon atoms inclusive, and wherein at least one of R_4 and R_5 have an aliphatic hydrocarbyl moiety having from about 12 to about 24 carbon atoms inclusive. These triglycerides are available from a variety of plants or their seeds and are commonly referred to as vegetable oils. R_6 and R_7 are independently a hydrogen, an aliphatic hydrocarbyl moiety having one to four carbon atoms, or the following formula:

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wherein x is an integer of about 0 to about 6, and wherein R_8 is an aliphatic hydrocarbyl moiety having four to 24 carbon atoms.

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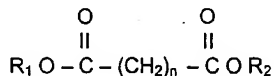
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Methods to produce the above transesterified vegetable oils are disclosed in U. S. Patent No. 6,278,006, which is incorporated in its entirety herein. Other triacylglycerol oils that may be used are disclosed in U. S. Patent Nos. 5,990,055 and 6,281,375, which are incorporated by reference in their entirety. The transesterified vegetable oil may include the glycerol polyol ester (shown above) alone or the non-glycerol polyol ester (shown above) alone, or a mixture of both.

Vegetable oils tend to crystallize at low temperature because the triacyl structures tend to be quite regular and subject to packing. This causes the viscosity to abruptly increase at lower temperatures, resulting in the failure of gelation index tests. To meet the gelation index requirement of less than about 12 as specified by the GF-3/API SL bench test specification, a low gelation index saturated synthetic ester (which is different from the vegetable oil) is added. For example, from about 10 to about 30% of a saturated synthetic ester was blended in the formulation. It was discovered that the synthetic ester, particularly saturated esters, lowered the gelation index significantly. The synthetic ester may be a dibasic ester such as adipate, a sebacate ester, a tribasic ester such as trimethylol ethane (TME), a trimethylol propane (TMP) ester, or a polyol ester, such as pentaerythritol ester. Preferably, the gelation index of the first ester added to the transesterified triglyceride oil should be less than about 10, less than about 8, or less than about 6. In some embodiments, the first ester used to lower the gelation index of the lubricant has a gelation index of less than about 5, such as about 4 or less, about 3 or less, about 2 or less, or about 1 or less.

Dibasic or dibasic acid esters are the products from a C₄-C₁₂ dicarboxylic acid (such as succinic, glutaric acid, adipic acid, and sebacic acid) reacting with 2 moles of C₁-C₁₂ alcohols. One example is di(2-ethylhexyl)adipate. The dibasic ester should have a viscosity index of at least about 120 in order to function adequately. Dibasic esters are of the formula:



wherein R₁ and R₂ are a hydrocarbyl group having from about 1 to about 20 carbon atoms and n is an integer from about 1 to about 20. A preferred dibasic ester is EMKARATE 1130™ which is the diester of a C₁₀ alcohol with sebacic acid by

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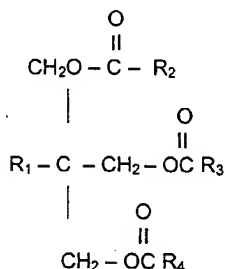
UNIQEMA PERFORMANCE CHEMICALS (New Castle, DE). R_1 and R_2 may be different moieties or the same moieties.

Dibasic esters having similar characteristics as those in the following table are also useful:

Property	Value
Flash Point, °C	230 (closed cup) 260 (open cup)
Auto Ignition Temperature, °C	385
Density, g/ml	0.909
Pour Point, °C	-60
Kinematic Viscosity, cSt	20.2 @ 40 °C 4.8 @ 100 °C

5 Tribasic esters are the products from a C_4 - C_{12} tricarboxylic acid reacting with 3 moles of C_1 - C_{20} alcohols or made by a fatty acid condensing with a polyol (tri-ol). The tribasic ester should have a viscosity index of at least about 120 in order to function adequately. Tribasic esters are of the formula:

10



15

wherein R_1 , R_2 , R_3 and R_4 are a hydrocarbyl group having from about 1 to about 20 carbon atoms. A preferred tribasic ester is EMKARATE 1550™ made by UNIQEMA

20 PERFORMANCE CHEMICALS (New Castle, DE). R_1 , R_2 , R_3 and R_4 may be different moieties or the same moieties.

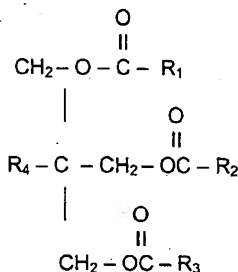
Other synthetic esters have the following formula:

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10 wherein R_1 , R_2 , R_3 , and R_4 are a hydrocarbyl group having from about 1 to about 20 carbon atoms. When R_4 is CH_3 , the resulting synthetic ester is a trimethylol ethane ester. When R_4 is CH_3CH_2 , the resulting synthetic ester is a trimethylol propane ester. Other suitable synthetic esters include EMKARATE 1700™ which is a pentaerythritol ester of a C_5 - C_7 alcohol, PRIOLUBE 3960™, PRIOLUBE 3939™, PRIOLUBE 1831™
 15 which are polymers made from a dimer acid with a di-alcohol by UNIQEMA PERFORMANCE CHEMICALS (New Castle, DE.) R_1 , R_2 , R_3 and R_4 may be different moieties or the same moieties.

To increase the viscosity at higher temperatures, viscosity index improvers were added to the formulation. Generally speaking, there are two types of viscosity modifier
 20 (or viscosity index improver). One is the relative polar ester-type, such as LUBRIZOL 7671™, which is a long chain ester of maleic anhydride styrene copolymer (see also, LUBRIZOL 7764™ and LUBRIZOL 7783™ which are polymethacrylate copolymers). The other is the non-polar hydrogenated olefin copolymer (OCP) type, such as LUBRIZOL 7075™, (also included are hydrogenated styrene-diene copolymers, such as
 25 INFINEUM SV 200™ and INFINEUM SV 150™, etc.) which are amorphous hydrocarbon polymers. Both of these viscosity modifiers were tested in the formulations.

By combining polar and non-polar types of viscosity modifiers, a wide range of viscosity grades of motor oils can be blended. Further, when blended with the synthetic
 30 esters, a motor oil is produced meeting the desired viscosity, gelation index specifications, and other specifications needed to make a renewable, environmentally friendly engine lubricant.

A preferred polar ester-type viscosity modifier is LUBRIZOL™ 7671 made by LUBRIZOL (Wickliffe, OH). LUBRIZOL™ 7671 is a polymethacrylate type thickener
 35 and also acts as a pour point depressant for vegetable oils. Other polar ester-type

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viscosity modifiers include LUBRIZOL™ 7764, LUBRIZOL™ 7776, LUBRIZOL™ 7785, LUBRIZOL™ 7786, from LUBRIZOL (Wickliffe, OH) which are polymethacrylate copolymer viscosity index improvers.

5 Polar ester-type viscosity modifiers having similar properties as those in the following table are also useful:

Property	Value
Flash Point, °C	165
Specific Gravity	0.90
Viscosity, cSt	8500 @ 40 °C 1500 @ 100 °C

A preferred non-polar hydrogenated olefin copolymer-type viscosity modifier is the LUBRIZOL 7075™ Series made by LUBRIZOL (Wickliffe, OH). This series is Lubrizol's next generation nondispersant olefin copolymer (OCP) viscosity modifier. Hydrogenated olefin copolymers are the most widely used type of viscosity modifier for
10 passenger car motor oils and heavy-duty diesel engine oils. Developed in the mid-1960s, hydrogenated olefin copolymers differ mainly in molecular weight and the ratio of ethylene to propylene. These polymers effectively minimize viscosity variations over typical engine operating temperatures. They are cost-effective and are suitable for formulating nearly any mainline engine oil. The polymers provide a cost-effective way
15 to meet the latest international and original equipment manufacturer (OEM) specifications for passenger car and heavy-duty diesel engine oils.

Non-polar hydrogenated olefin copolymer-type viscosity modifiers having the following characteristics may also be useful in embodiments:

Property	Value
Flash Point, °C	190
Specific Gravity	0.87
Viscosity, cSt	825 @ 100 °C

LUBRIZOL 7075D™ is a preferred olefin copolymer type viscosity modifier
20 from LUBRIZOL (Wickliffe, OH). Other olefin copolymer type viscosity modifiers include the LUBRIZOL 7070™ series, 7077™ series, 7740™ series; INFINEUM SV140™, SV145™, SV200™, SV205™, SV300™, SV305™, (EXXONMOBIL, TX) and PARATONE™ 8900 series by (CHEVRON,CA).

The ester type viscosity modifiers contribute to the lowering of the gelation
25 index. Using LUBRIZOL™ 7764 and LUBRIZOL™ 7785, the maximum amount of ester viscosity modifiers allowable in the formulation without failing the gelation index specification is from about 1.7 to about 2.0%, see Fig. 1. At this low concentration of

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the ester type viscosity modifier alone, the viscosity grade of the formulated oil is a SAE 30 grade or lower.

Ester type viscosity modifiers having the following characteristics may also be useful in embodiments:

Property	Value
Flash Point, °C	161
Specific Gravity	0.90
Viscosity, cSt	20.5 @ 100 °C

5 The solubility of the hydrogenated olefin copolymer-type viscosity modifier in vegetable oil is about 4 to about 6 wt% due to the polarity difference. When using the hydrogenated olefin copolymer-type viscosity modifier alone, the formulation of the lubricant is a viscosity grade SAE 30 grade oil.

10 However, a combination of these two types of viscosity modifiers produces a wide range of viscosity grades of motor oils. Further, when combined with the vegetable oil and the synthetic ester, a motor oil was produced meeting the desired viscosity, gelation index specifications, and other bench test specifications. The ester type viscosity index improver may be added in an amount from about 0 to about 3.0%, more preferred from about 0.2 to about 2.5%, most preferred from about 0.5 to about 2% and the
15 hydrogenated olefin copolymer type viscosity index improver may be added in an amount from about 0 to about 6.0%, more preferred from about 1 to about 5%, most preferred from about 2 to about 4%.

Other suitable conventional viscosity index improvers, or viscosity modifiers, are olefin polymers, such as polybutene, hydrogenated polymers and copolymers and
20 terpolymers of styrene with isoprene and/or butadiene, polymers of alkyl acrylates or alkyl methacrylates, copolymers of alkyl methacrylates with N-vinyl pyrrolidone or dimethylaminoalkyl methacrylate. These are used as required to provide the viscosity range desired in the finished oil, in accordance with known formulating techniques.

25 Esters obtained by co-polymerizing styrene and maleic anhydride in the presence of a free radical initiator and thereafter esterifying the copolymer with a mixture of C₄-C₁₈ alcohols, are also useful as viscosity modifying additives. The styrene esters generally are considered to be multi-functional premium viscosity modifiers. The styrene esters in addition to their viscosity-modifying properties also are pour point depressants and exhibit dispersancy properties when the esterification is terminated before its
30 completion leaving some unreacted anhydride or carboxylic acid groups. These acid

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groups can then be converted to amides by reaction with a primary amine. The copolymerization of styrene with maleic anhydride creates a copolymer (SMA) which has a higher glass transition temperature than polystyrene and is chemically reactive with certain functional groups. Thus, SMA polymers are often used in blends or composites
5 where interaction or reaction of the maleic anhydride provides for desirable interfacial effects. Some SMA polymers that are commercially available from ROHMAX USA (Horsham, PA) include VISCOPLEX™ 2-360, VISCOPLEX™ 2-500, VISCOPLEX™ 3-540, VISCOPLEX™ 4-671, and VISCOPLEX™ 6-054.

One difference between mineral oil and vegetable oil is that the former is
10 predominantly non-polar hydrocarbons whereas the latter has polar ester functional groups. There is lack of dispersant/inhibitor (DI) packages formulated specially for use with the more polar vegetable oils. Therefore, conventional DI packages were used in embodiments of the formulation. In order to solubilize conventional DI packages in vegetable oil, about 10 to about 30% of API Group I to Group III mineral oils or Group
15 IV poly- α -olefin (PAO) synthetic oils are blended with the vegetable oil to lower the polarity. The resulting oils are clear and homogeneous.

A dispersant/inhibitor additive package may be added to the lubricant to break insoluble particles already formed and to inhibit the formation of particles. Particles are kept finely divided so that they can remain dispersed or colloiddally suspended in the oil.
20 The dispersant/inhibitor additive package is preferably in an amount from about 6 to about 18 wt%, more preferred from about 8 to about 16 wt%; and most preferred from about 10 to about 14 wt%.

Detergents and dispersants are polar materials that serve a cleaning function. Detergents include metal sulfonates, metal salicylates and metal thiophosphonates.
25 Dispersants include polyamine succinimides, hydroxy benzyl polyamines, polyamine succinamides, polyhydroxy succinic esters and polyamine amide imidazolines. Detergents are generally combined with dispersant additives in crankcase oils. Detergents chemically neutralize acidic contaminants in the oil before they become insoluble and fall out of the oil, forming a sludge. Neutral or basic compounds are
30 created which can remain in suspension in the oil. Lubricating oils typically contain from about 2 to about 5 wt% of detergent.

Suitable ashless dispersants may include, but are not limited to, polyalkenyl or borated polyalkenyl succinimide where the alkenyl group is derived from a C₃-C₄ olefin,

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especially polyisobutenyl having a number average molecular weight of about 7,000 to 50,000. Other well known dispersants include the oil soluble polyol esters of hydrocarbon substituted succinic anhydride, e.g. polyisobutenyl succinic anhydride, and the oil soluble oxazoline and lactone oxazoline dispersants derived from hydrocarbon substituted succinic anhydride and di-substituted amino alcohols, post-grafted polymers of ethylenepropylene with an active monomer such as maleic anhydride which may be further reacted with alcohol or an alkylene polyamine, styrene-maleic anhydride polymers post-reacted with alcohols and amines and the like.

Dispersants typically contain a hydrocarbon chain attached to an amine or alcohol-containing polar group. The hydrocarbon "tail" serves to solubilize the molecule in the lubricant base stock, while the polar group serves to attract the polar contaminants resulting from the lubricant breakdown. The dispersant forms millions of micellar structures in the lubricant base stock which contain a highly polar core and disperse enormous amounts of polar contaminants. These contaminants are products of oxidation which serve as precursors to varnish/carbon/sludge formation as well as already-formed varnish/carbon/sludge deposits. The dispersed contaminants are held in "solution" in the basestock while already-formed deposits are cleaned off the metal and elastomer surfaces. Both the suspended precursors and deposits readily pass through commonly used filters. Ultimately, when these cores are saturated, the dispersant can no longer pick up contaminants, so the oil must be drained. However, the oil is usually drained well before this happens.

Lubricant oxidation is a chain reaction caused by the reaction of the oxygen in air with the lubricant base stock. Oxidation results in the formation of high molecular weight oil-insoluble polymers. These can settle out as sludges, varnishes and gums. They also cause an increase in the viscosity of the lubricant. The function of the inhibitors is the prevention of the deterioration from the oxygen attack on the lubricant. The oxidation inhibitors function either to destroy free radicals (phenolics or amines) or to decompose the peroxides (amines or ZDDPs) which are involved in the oxidation mechanism. As a result, the lubricant retains its cleanliness and viscosity allowing it to function properly over its drain interval.

A preferred dispersant/inhibitor additive package is LUBRIZOL 9850U™ from LUBRIZOL (Wickliffe, OH), or LUBRIZOL 9850™. The contents of DI packages are generally a proprietary secret, but usually contain an antiwear agent, such as ZDDP

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(Zinc dialkyl dithiophosphate); an antioxidant- phenolic and/or amine type antioxidant; a detergent (Mg and/or Ca sulfonate or phenate); a dispersant (polyisobutylene succinamide); a corrosion inhibitor; a rust inhibitor, a friction modifier; an anti-foaming agent, etc. Other suitable dispersant/inhibitor additive packages for gasoline and diesel engine oils are ORONITE™ (CHEVRON, CA) and INFINEUM™ (EXXON-MOBIL, TX). GF-3 DI packages include, for example, OLOA 55007™ and OLOA 59029™ (CHEVRON, CA), INFINEUM 5063™, INFINEUM 3421™, INFINEUM 3422™ (EXXON-MOBIL, TX), and LUBRIZOL 20,000™ and LUBRIZOL 20,000A™ (LUBRIZOL, OH).

10 Dispersant/inhibitor additive packages having similar characteristics as those listed below are also be useful:

Property	Value
Flash Point, °C	146-167
Specific Gravity	0.96 - 0.97
Viscosity, cSt	1350-1400 @ 40 °C 100-125 @ 100 °C

The environmentally friendly lubricant may further include one or more additives. Such additives include, but are not limited to antioxidants, pour point depressants, detergents, dispersants, friction modifiers, rust inhibitors, corrosion inhibitors and anti-foaming agents.

15 Typical antioxidants are aromatic amines, phenols, compounds containing sulfur or selenium, dithiophosphates, sulfurized polyalkenes, and tocopherols. Hindered phenols are particularly useful, and include for example, 2,6-di-tert-butyl-p-cresol (DBPC), tert-butyl hydroquinone (TBHQ), cyclohexylphenol, and p-phenylphenol.

20 Example of amine-type antioxidants include phenyl- α -naphthylamine, alkylated diphenylamines and unsymmetrical diphenylhydrazine. Zinc dithiophosphates, metal dithiocarbamates, phenol sulfides, metal phenol sulfides, metal salicylates, phospho-sulfurized fats and olefins, sulfurized olefins, sulfurized fats and fat derivatives, sulfurized paraffins, sulfurized carboxylic acids, disalicylal-1,2-propane diamine, 2,4-

25 bis (alkyldithio)-1,3,4-thiadiazoles) and dialauryl selenide are examples of useful antioxidants. IRGANOX L-64 (Ciba Specialty Chemicals, Tarrytown, NY) provides a mixture of antioxidants that is particularly useful. Antioxidants are typically present in amounts from about 0.001 to about 10 weight %. In preferred embodiments, from about 0.01% to about 3.0% of an antioxidant is added to the lubricant. U. S. Patent Nos.

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5451334 and 5773391 further disclose additional antioxidants and are hereby incorporated in their entirety by reference.

Pour point depressants (PPD) lower the pour point of petroleum products containing wax by reducing the tendency of the wax to collect into a solid mass. Pour point depressants permit flow of the oil formulation below the pour point of the unmodified lubricant. Common pour point depressants include polymethacrylates, wax alkylated naphthalene polymers, wax alkylated phenol polymers and chlorinated polymers. U. S. Patent Nos. 5451334 and 5413725 further disclose additional pour point depressants and are hereby incorporated in their entirety by reference.

Pour point depressants are used generally in amounts of from about 0.01 to about 5 wt%, more typically from about 0.1 to about 1 wt%. Illustrative of pour point depressants which are normally used in lubricating oil compositions are polymers and copolymers of n-alkyl methacrylate and n-alkyl acrylates, copolymers of di-n-alkyl fumarate and vinyl acetate, alpha-olefin copolymers, alkylated naphthalenes, copolymers or terpolymers of alpha-olefins and styrene and/or alkyl styrene, styrene dialkyl maleic copolymers and the like. A preferred pour point depressant is ACRYLOID 3004 Oil Additive available by ROHMAX USA (Horsham, PA) that uses the commercial name VISCOPLEX 1-3004™. The chemistry is based on polymethacrylate (PMA). Other VISCOPLEX series 1 wax modifiers that can be used include VISCOPLEX 1-6004, VISCOPLEX 1-331, and VISCOPLEX 1-600. The VISCOPLEX series 10, such as VISCOPLEX 10-130, and 10-171 can also be used.

Suitable metal detergent additives are known in the art and may include one or more of overbased oil-soluble calcium, magnesium and barium phenates, sulfurized phenates, and sulfonates (especially the sulfonates of C₁₆-C₅₀ alkyl substituted benzene or toluene sulfonic acids which have a total base number of about 80 to 300). These overbased materials may be used as the sole metal detergent additive or in combination with the same additives in the neutral form; but the overall metal detergent additive should have a basicity as represented by the foregoing total base number. Preferably they are present in amounts of from about 3 to about 6 wt% with a mixture of overbased magnesium sulfurized phenate and neutral calcium sulfurized phenate (obtained from C₉ or C₁₂ alkyl phenols).

Suitable anti-wear additives are oil-soluble zinc dihydrocarbyldithiophosphates with a total of at least 5 carbon atoms and are typically used in amounts from about 1 to

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about 6 wt% by weight. Other anti-wear additives include dithiophosphates and in particular, zinc dialkyl dithiophosphates, metal sulfonates, metal phenate sulfides, fatty acids, acid phosphate esters and alkyl succinic acids. Anti-wear additives adsorb on metal, and provide a film that reduces metal-to-metal contact. In general, anti-wear additives include zinc dialkyldithiophosphates, tricresyl phosphate, didodecyl phosphite, sulfurized sperm oil, sulfurized terpenes and zinc dialkyldithiocarbamate.

Rust inhibitors protect surfaces against rust and include alkylsuccinic type organic acids and derivatives thereof, alkylthioacetic acids and derivatives thereof, organic amines, organic phosphates, polyhydric alcohols, and sodium and calcium sulphates. Rust inhibitors are employed in very small proportions such as from about 0.1 to about 1 wt% with suitable rust inhibitors being exemplified by C₉-C₃₀ aliphatic succinic acids or anhydrides such as dodecenyl succinic anhydride.

Anti-foam additives reduce or prevent the formation of a stable surface foam and are typically present in amounts from about 0.01 to about 1 wt%. Polymethylsiloxanes, polymethacrylates, salts of alkylene dithiophosphates, amyl acrylate telomer and poly(2-ethylhexylacrylate-co-ethyl acrylate) are non-limiting examples of anti-foam additives.

Additionally, by mixing high and low viscosity mineral oils in the formulation, it was possible to prepare a full range of SAE grade motor oils. Viscosity of an automotive oil is classified in SAE (Society of Automotive Engineers) viscosity grades represented by numbers such as 30, 40, 50. The higher the number, the thicker the oil and the greater its effectiveness in high temperature operations. Lower numbered oils that are thinner oils with low viscosity are used in cold climates as they flow more easily and are identified by a "W" mark next to the grade of oil on the package. Multigrade oils 5Wxx, 10Wxx, 20Wxx, etc. are suitable for both low and high temperature conditions. Lubricating oils made specifically for industrial use have their viscosity classified by ISO (international Organization for Standardization) grades.

To prepare a wide range of SAE grade motor oils, high and low viscosity mineral oils are added to the environmentally friendly lubricant. The SAE grade motor oils that can be achieved include 0W-30, 5W-30, 10W-30, and 10W-40. Mineral oils from Group I to Group V are preferred. Preferred examples useful in the formulation include:

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Table 4: Mineral Oils

Group	Example	Kin. Visc. @ 40°C (cSt)	Kin. Visc. @ 100°C (cSt)	VI
II	EXCEL 100-HC™	20.85	4.2	101
II	EXCEL 230-HC™	42.5	6.4	100
II	EXCEL 575-HC™	111	12.3	100
III	Yubase 150N™	37.9	6.6	129
III	Yubase 240N™	47.4	7.7	129
III	CHEVRON UCBO7R™	28.2	6.8	137
III	SHELL XHVI™	47.3	8.2	148

- EXCEL 100-HC™, 230-HC™, and 575-HC™ are Group II mineral oils made by PENNZOIL-QUAKER STATE COMPANY (Houston, TX). Yubase 150N™ and 240N™ are Group III mineral oils made by Yukong (Seoul, Korea). CHEVRON UCBO7R™ is a Group III mineral oil made by CHEVRON. SHELL XHVI™ is a Group III mineral oil made by Shell Chemical Company. Mineral oils are used generally in amounts of from about 0 to about 40 wt%.

- The following examples exemplify embodiments of the invention. They do not limit the invention as otherwise described and claimed herein. All numbers in the examples are approximate values.

EXAMPLE 1

- Table 5A and Table 5B provide the formulations and physical properties of lubricants using polar ester-type viscosity modifiers. Formulations A to C used LUBRIZOL 7764™, which is a polymethacrylate copolymer, and formulations D to F used LUBRIZOL 7785™ which is a polymethacrylate copolymer dispersed in vegetable oil. The dispersant/inhibitor package was LUBRIZOL 9850U™. The pour point depressant was Viscoplex 1-3004™. The mineral oil was Yubase 150N™ and the synthetic ester was Emkarate 1130™. The vegetable oil was AGRI-PURE 560™.

Table 5A: Formulations A-F

Formulation		A	B	C	D	E	F
Component	Description	Wt %	Wt %	Wt %	Wt %	Wt %	Wt %
Lubrizol 7764™	VII	1	1.5	2	0	0	0
Lubrizol 7785™	VII	0	0	0	1	2	3
Lubrizol 9850U™	DI	12	12	12	12	12	12
Viscoplex 1-3004™	PPD	0.1	0.1	0.1	0.1	0.1	0.1
Yubase 150N™	Group III oil	25	25	25	25	25	25
Emkarate 1130™	Dibase ester	20	20	20	20	20	20
AGRI-PURE 560™	Modified vegetable oil	balance	balance	balance	balance	balance	balance
Total wt%		100	100	100	100	100	100

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Table 5B: Properties of Formulations A-F

Physical Properties	A	B	C	D	E	F
KV @ 100°C, cSt	8.7	9.32	10.02	8.79	10.25	11.36
KV @ 40°C, cSt	43	46.3	49.5	43.4	50.8	64.7
VI	187	190	195	187	195	171
Gelation Index	5.7	8.2	10.5	10	20.9	25.7

The gelation index (Gi) for formulations including LUBRIZOL 7764™ and LUBRIZOL 7785™ were plotted against the weight percent of viscosity modifier (VII) as shown in Figure 1. This graph indicates that when the amount of viscosity modifier was higher than about 2.2 wt % and about 1.2 wt % of LUBRIZOL 7764™ and LUBRIZOL 7785™, respectively, formulations failed the GF-3/API SL specification of the gelation index maximum of 12. When using less than 2.2 wt % of LUBRIZOL 7785™ the formulations passed the gelation index, but the finished oils were limited to the SAE 30 viscosity grade. Similarly, using lower than 1.2 wt % of LUBRIZOL 7764™ gave formulations that passed the gelation index of 12, but the finished oils were limited to the SAE 20 viscosity grade.

EXAMPLE 2

The following formulations in Table 6A were prepared using an olefin copolymer type viscosity modifier, LUBRIZOL 7075D™ in place of the polar-ester type viscosity modifier used above. The physical properties of these formulations are provided in Table 6B. The formulations were clear and homogeneous at ambient temperature. However, when attempting to measure the gelation index in formulations G and H according to the ASTM D 5133 procedure, the viscosity modifier was found to separate and stick to the wall of the test cell during the chilling process, whereas formulation I stayed clear and homogeneous. This suggested that the formulation using the olefin copolymer type viscosity modifier, LUBRIZOL 7075D™, may be limited to about 0 to about 6 wt % in the formulation.

Table 6A: Formulations G-I

Formulation		G	H	I
Components	Description	Wt%	Wt%	Wt%
Lubrizol 7075D™	VII	6.3	7.98	3.94
Lubrizol 9850U™	DI	12	12	12
Viscoplex 1-3004™	PPD	0.1	0.1	0.1
Excel 100-HC™	Group II oil	0	25	0
Excel 230-HC™	Group II oil	25	0	0
Excel 575-HC™	Group II oil	0	0	25
Emkarate 1130™	Dibase ester	20	20	20
AGRI-PURE 560™	Modified vegetable oil	balance	balance	balance
Total wt%		100	100	100

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Table 6B: Properties of Formulations G-I

Physical Properties	G	H	I
KV @ 100°C, CST	10.3	10.3	10.3
KV @ 40°C, CST	54.6	51.9	55.9
VI	179	192	174
CCS @ -25°C	2390	1830	3270
CCS @ -30°C	N/A	1027	6060
MRV TP-1 @ -35°C	9100	6600	14100
MRV YS @ -35°C	0	0	0
Scanning Brookfield Temp.			
@30,000 cp.	N/A	N/A	-31.9°C
@ 40,000 cp.	N/A	N/A	-34°C
Gelation Index	N/A	N/A	6
Gelation Temp., °C	N/A	N/A	-12°

- Formulation I is an SAE 30 grade lubricant. It is possible to raise the viscosity of Formulation I to SAE 40 grade by increasing the non-biodegradable heavy oil, such as
- 5 Excel 575-HC, which would decrease the biodegradability of the formulation.

EXAMPLE 3

- Table 7A represents blends using a combination of the ester-type and the olefin copolymer type viscosity modifiers in a base oil comprising Group III mineral oils (Yubase 150N™ and Yubase 240N™), a dibasic ester, and modified vegetable oil
- 10 (AGRI-PURE 560™). Table 7B discloses the physical properties of the oils in Table 7A. These formulations pass the GF-3/API SL gelation index specification of less than about 12 and meet other physical properties of a SAE 5W-30 grade oil.

Table 7A: Formulations J-L

Formulation		J	K	L
Component	Description	wt %	wt %	wt %
Lubrizol 7785™	VII	1	0	0
Lubrizol 7764™	VII	0	1.7	1.7
Lubrizol 7075D™	VII	3.28	1.89	1.4
Lubrizol 9850U™	DI	12	12	12
Viscoplex I-3004™	PPD	0.1	0.1	0.1
Yubase 150N™	Group III Oil	25	25	0
Yubase 240N™	Group III Oil	0	0	25
Emkarate 1130™	Dibase Ester	20	20	20
AGRI-PURE 560™	Vegetable Oil	balance	balance	balance
Total wt%		100	100	100

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Table 7B: Properties of Formulations J-L

Physical Properties	Test Method	J	K	L
KV @ 100°C	D-445	10.3	10.5	10.53
KV @ 40°C	D-445	51.8	52.9	53.52
VI	D-2270	193	194	191
Pour Point, °C	D-5950	-47°C	-47°C	-45°C
CCS @ -30°C	D-5293	-	3540	-
CCS @ -25°C	D-5293	2050	2090	2230

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Physical Properties	Test Method	J	K	L
HTHS Viscosity, cP @ 150°C	D-4683	3.42	3.37	3.37
MRV TP-1 @ -35°C	D-4684	-	9800	10400
MRV YS @ -35°C	D-4684	-	0	0
MRV TP-1 @ -30°C	D-4684	3800	4600	4800
MRV YS @ -30°C	D-4684	0	0	0
Scanning Brookfield Temp.	D-5133			
@30,000 cP		-31.5°C	-33.4°C	-31.4°C
@ 40,000 cP		-32.6°C	-34.1°C	-32.2°C
Gelation Index	D-5133	10.4	10.4	10.9
Gelation Temp., °C	D-5133	-31°C	-34°C	-32.2°C
NOACK volatility, Wt % Loss	D-5800	N/A	7.8	N/A
% off at 700°C (Sim. Dist.)	D-2687	N/A	5.1	N/A

EXAMPLE 4

- Formulation K was submitted to independent testing laboratories for ASTM D-6335 Thermo-Oxidation Engine Oil Simulation Test (TEOST), and ASTM D-5864-95 Biodegradability tests were performed at BfB Oil Research in Belgium. Results are shown in Table 8. TEOST may be useful in determining the piston deposit control capability of the motor oil. According to the GF-3/API SL specification the total deposit in TEOST is 45 mg maximum. According to the ASTM D-5964-95 biodegradability test, if the carbon dioxide released is higher than 60% (within 28 days), the material is qualified as easily biodegradable.

Table 8: Formula K

Test	Test Method	K
TEOST, Total Deposit	D-6335	11.6 mg
Biodegradability	D 5864-95	62%

EXAMPLE 5

- To reduce the cost of the lubricants, Group III mineral oils in Example 3 can be replaced by Group II mineral oils, such as Excel HC or Exxon HC (hydro-conversion) oils. Table 9A discloses formulations, in which the different viscosity grades of Group II oils were used alone or in combination to make wide viscosity ranges of motor oils. Table 9B shows the properties of the formulations. To enhance the oxidative stability, additional antioxidants (i.e. Irganox L-64™) can be added to the formulation as illustrated in the formulation Q. Formulation R replaces the Irganox L-64™ with NAUGALUBE MOLYFM 2543™ (Crompton Corporation, Middlebury, CT) which is a multifunctional friction modifier, anti-wear, and antioxidant additive.

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Table 9A: Formulations M-R

Formulation		M	N	O	P	Q	R
SAE Grade		0W-30	5W-30	10W-30	10W-40	10W-40	10W-30
Components	Description	wt %	wt %	wt %	wt %	wt %	wt %
DI, Lz 9850U	DI	12	12	12	12	12	12
Viscoplex 1-3004	PPD	0.1	0.1	0.1	0.1	0.1	0.1
Lz 7764	VII	1.7	1.2	1.1	1.7	1.7	0
Lz 7075D	VII	3.3	1.5	0	3.3	3.3	3.3
Excel 100-HC	Group II Oil	25	10	0	0	0	25
Excel 575-HC	Group II Oil	0	20	30	30	29.5	0
Irganox L-64	Antioxidant	-	-	-	-	0.5	-
Emkarate 1130	Dibase ester	20	20	20	20	20	20
Naugalube MolyFM 2543	Friction modifier Antioxidant	-	-	-	-	-	0.5
Cargill AP-560	Modified vegetable oil	balance	balance	balance	balance	balance	balance
Total wt%		100	100	100	100	100	100

Table 9B: Properties of Formulations M-R

Physical Properties	M	N	O	P	Q	R
SAE Grade	0W-30	5W-30	10W-30	10W-40	10W-40	10W-30
KV @ 100°C	10.03	10.15	10.28	13.42	13.5	9.9
KV @ 40°C	49.3	54.8	57.8	77.7	78.8	55.6
VI	196	176	168	177	176	165
Pour Point, °C	-45	-51	-33	-45	< -50	< -54
CCS @ -30°C	3220	-	-	-	-	-
CCS @ -25°C	-	2860	-	-	4260	3550
CCS @ -20°C	-	-	2160	2330	2510	2020
HTHS Viscosity, cP @ 150°C	3.27	3.37	3.43	4	4.08	3.4
MRV TP-1 @ -40°C	17,600	-	-	-	-	-
MRV YS @ -40°C	0	-	-	-	-	-
MRV TP-1 @ -35°C	-	14,000	-	-	-	17,800
MRV YS @ -35°C	-	0	-	-	-	0
MRV TP-1 @ -30°C	-	-	7,600	11,300	10,000	-
MRV YS @ -30°C	-	-	0	0	0	-
Scanning Brookfield Temp.						
@ 30,000 cP	-33.8°C	-31.7°C	-33.2°C	-27.7°C	-30.5°C	-28.7°C
@ 40,000 cP	-35.1°C	-32.4°C	-36.5°C	-29.4°C	-31.4°C	-30.4°C
Gelation Index	9.4	8.4	7.8	7.3	8.4	6.2
Gelation Temp., °C	-34	-33	-25	-7	-32	-10
NOACK volatility, Wt % Loss	12.8	9.29	6.66	7.2	7.2	8.2
% off at 700°C (Sim. Dist.)	9.8	4.7	3.1	3.7	6.1	5.1

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EXAMPLE 6

The formulation Q was submitted to PerkinElmer Automotive Research Laboratory (San Antonio, TX) for high temperature TEOST MHT-4 Thermo-Oxidation Engine Oil Simulation test, Homogeneity and Miscibility (H&M) test, Foam sequence I, II, and III test, High Temperature Foam test, EOFT (Engine Oil Filterability test), and

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EOWTT (Engine Oil Filterability/water tolerance test). In the H&M test, the tested oil shall remain homogeneous and miscible when mixed with SAE reference oils. Table 10 discloses the results. According to ASTM D 4485-99b, the oil meets the bench test of API SL minimum performance standard.

5

Table 10: Formula Q

Description of the Test	Test Method	Test Result	GF-3 Limit
H&M (Homogeneity & Miscibility) Test	FTM-3470.1	non-separation	non-separation
TEOST MHT 4,	D 6335M	/	/
Total Deposit (Rod + Filter)		21.6 mg	45 mg (max)
Foam Test GF-3	D 892	/	/
Sequence I, foaming/setting		0/0	10 max./0
Sequence II, foaming/setting		0/0	50 max./0
Sequence III, foaming/setting		0/0	10 max./0
High Temperature Foam Test	D 6082	/	/
Foam Tendency		20 ml.	100 ml (max)
Foam Stability		0 ml	0
EOFT (Engine Oil Filterability Test),	GM 9099P	/	/
% Flow Reduction		24.82	50 (max)
EOWTT (Engine Oil Filterability/Water Tolerance Test)	GM 9099P	/	/
with 0.6% water		19.69	50 (max)
with 1.0% water		15.53	50 (max)
with 2.0% water		17.05	50 (max)
with 3.0% water		12.36	50 (max)
Gelation Index	D 5133	8.4	12 (max)

EXAMPLE 7

The R formulation was tested by a modified ASTM Sequence VI B Fuel Economy test in a Ford V-8 4.6 L engine mounted on a dynamometer as follows:

1. The engine was drained of existing oil and a 6-qt. quantity of test oil was run for 10 minutes with a fresh filter.
2. The engine was allowed to drain and a new oil filter and another 6 quarts of test oil was installed.
3. The engine was then started and an aging cycle was initiated 10 seconds later.
4. The aging cycle was designed to mimic that of the sequence VI B aging with the following parameters: 1500 rpm, 71.4 ft. lbs. torque (load) for 7320 seconds, 18.9 ft. lbs. torque for 1920 seconds, 71.4 ft. lbs. torque for 100 seconds (total aging 9340 seconds), 212°F coolant temperature, and 220°F oil temperature.

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5. At completion of the aging cycle, the highway cycle was conducted after exactly 5 minutes of a 600 rpm idle with no load.

6. Following the highway cycle, a metro (city) cycle was initiated after exactly 5 minutes of a 600 rpm idle with 0 load.

5 7. Following the metro cycle, the engine was stopped and test oil was drained and samples were taken at that time. Cooling water temperatures (4000 gallon engine water tank) were consistent on each day of testing at 83°F. Vapor pressure, fuel specific gravity and relative humidity were recorded and entered into the dynamometer prior to each day's test sequence.

10 The Highway cycle consisted of a 300 second cycle programmed as follows: minimum rpm: 850, maximum rpm 1840, load varied from: 5 to 28 ft. lbs. The Metro cycle consisted of a 504 second, low rpm and load cycle programmed as follows: minimum rpm: 560, maximum rpm: 1320, load varied from: 0 to 40 ft. lbs. Emissions readings were taken beginning at the onset of each programmed test cycle and ran for
15 the entire duration of each.

The results show that as compared with a reference oil and a commercial 10W-30 oil, the R formulation reduced the emission, especially, the hydrocarbon exhaust gas as shown in Table 11.

Table 11: Formula R

Metro	Hydrocarbon, ppm	CO %	CO2 %	O2 %
Reference Oil	590	0.90	12.91	1.71
Commercial 10W30	308	1.20	12.89	1.50
Formula R	162	1.10	13.65	1.52
Highway				
Reference Oil	141	1.10	13.22	1.14
Commercial 10W30	207	1.00	13.21	1.18
Formula R	93	1.20	13.90	1.16
4-Hour Aging				
Reference Oil	117	0.90	13.40	0.94
Commercial 10W30	238	0.83	13.28	1.13
Formula R	111	0.86	14.08	1.09

20

EXAMPLE 8

Table 12 represents a range of SAE grade lubricant oils formulated from blends using a combination of the ester-type and the olefin copolymer type viscosity modifiers in a base oil comprising a blend of Group II mineral oils (Excel 100-HC™ and Excel
25 575-HC™), a dibasic ester, and CARGILL modified vegetable oil, AGRI-PURE 560™.

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The dispersant/inhibitor additive package was Oloa 55007 and the pour point depressant was Viscoplex 1-3004. Table 12 discloses the physical properties of the oils in Table 12. These formulations pass API SL gelation index specification of less than about 12 and meet other physical properties for their appropriate SAE grade.

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Table 12A: Formulations S-V

Formulation		S	T	U	V
SAE Grade		0W-30	5W-30	10W-30	10W-40
Components	Description	wt %	wt %	wt %	wt %
Lz 7764	VII	1.70	1.70	1.00	1.70
Lz 7075F	VII	3.50	3.50	2.40	3.80
Excel 100-HC	Group II Oil	20.00	15.00	0.00	0.00
Excel 575-HC	Group II Oil	0.00	5.00	30.00	29.00
Cargill AP560	Modified vegetable oil	45.54	45.54	37.34	36.24
Emkarate 1130	Dibase ester	20.00	20.00	20.00	20.00
Oloa 55007	DI	9.16	9.16	9.16	9.16
Viscoplex 1-3004	PPD	0.10	0.10	0.10	0.10
Total wt %		100.0%	100.0%	100.0%	100.0%

Table 12B: Properties of Formulations S-V

Physical Properties	S	T	U	V
SAE Grade	0W-30	5W-30	10W-30	10W-40
KV 100°C, cSt	9.62	10.0	10.9	13.1
KV 40°C, cSt	43.3	46.1	61.4	72.9
VI	215.8	211.6	171	181
CCS -35°C, cP	5420	6541	-	-
CCS -30°C, cP	3013	3290	6650	6734
CCS -25°C, cP	-	-	3530	3650
Scanning Brookfield Temp.				
@30000 cP	-34.9°C	-34.5°C	-30.5°C	-30.7°C
@40000 cP	-36.5°C	-35.9°C	-31.7°C	-31.4°C
GELATION INDEX	10.4	9.6	5.8	8.9
GELATION TEMP.	-34°C	-34°C	-33°C	-32°C

EXAMPLE 9

Table 13 represents a range of SAE grade lubricant oils formulated from blends using a combination of the ester-type and the olefin copolymer type viscosity modifiers in a base oil comprising a blend of Group II mineral oils (Excel 100-HC™ and Excel 575-HC™), a dibasic ester, and modified vegetable oil (AGRI-PURE 560™). The dispersant/inhibitor additive package was Lubrizol 20000 and the pour point depressant was Viscoplex 1-3004. Table 13B discloses the physical properties of the oils in Table 13A.

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Table 13A: Formulations W-Z

Formulation		W	X	Y	Z
SAE Grade		0W-30	5W-30	10W-30	10W-40
Components	Description	wt %	wt %	wt %	wt %
Lz 7764	VII	2.60	1.40	1.00	1.60
Lz 7075F	VII	1.40	1.40	1.00	2.50
Excel 100-HC	Group II Oil	25.00	5.00	0.00	0.00
Excel 575-HC	Group II Oil	2.00	20.00	30.00	30.00
Cargill AP560	Modified vegetable oil	36.90	40.10	35.90	33.80
Emkarate 1130	Dibase ester	20.00	20.00	20.00	20.00
Lubrizol 20000	DI	12.00	12.00	12.00	12.00
Viscoplex 1-3004	PPD	0.10	0.10	0.10	0.10
Total wt %		100.0%	100.0%	100.0%	100.0%

Table 13B: Properties of Formulations W-Z

Physical Properties	W	X	Y	Z
SAE Grade	0W-30	5W-30	10W-30	10W-40
KV 100°C, cSt	11.1	10.9	11.2	13.2
KV 40°C, cSt	51.9	58.69	61.7	75.2
VI	212	182	176	179
CCS -35°C, cP	5671	10390	-	-
CCS -30°C, cP	-	5160	6650	6734
CCS -25°C, cP	-	-	3530	3650

EXAMPLE 10

- 5 Table 14 represents a 5W-30 SAE grade lubricant oil formulation using a combination of the ester-type and the olefin copolymer type viscosity modifiers in a base oil comprising a blend of Group II mineral oils (Excel 100-HC™ and Excel 575-HC™), a dibasic ester, and modified vegetable oil (AGRI-PURE 560™). The dispersant/inhibitor additive package was Lubrizol 20000 and the pour point depressant was Viscoplex 1-
- 10 3004. To enhance performance, an extra antioxidant was added. This formulation passed all API SL bench test requirements. Table 14 also discloses the physical properties of the formulation.

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Table 14: Formulation and Physical Properties of Formulation AA

Formulation		AA
SAE Grade		5W-30
Components	Description	wt %
Lz 7764	VII	1.30
Lz 7075F	VII	1.2
Excel 100-HC	Group II Oil	5
Excel 575-HC	Group II Oil	19
Cargill AP560	Modified vegetable oil	40.40
Emkarate 1130	Dibase ester	20.0
Lubrizol 20000A	DI	12.00
Viscoplex 1-3004	PPD	0.1
Irganox L-64	Antioxidant	1.0
Total wt %		100.00%
Physical Properties		
Kin. Vis @ 100°C		10.94 cSt
@ 40°C		59.09 cSt
VI		180
CCS -35°C		12160 cP
CCS -30°C		6180 cP
TBS@ 150°C		3.5
Brookfield Temp		
@ 30,000 cP		-31.2°C
@ 40,000 cP		-32°C
Gelation Index		8.3
Gelation Temp.		-32°C
MRV TP-1 @ -35°C		15900 cP
MRV YS @ -35°C		0
Pour Point		< -52°C

EXAMPLE 11

- The formulation AA was submitted to PerkinElmer Automotive Research Laboratory (San Antonio, TX) for high temperature TEOST MHT-4 Thermo-Oxidation Engine Oil Simulation test, Homogeneity and Miscibility (H&M) test, Foam sequence I, II, and III test, High Temperature Foam test, EOFT (Engine Oil Filterability test), EOWTT (Engine Oil Filterability/water tolerance test), Gelation Index, NOACK Volatility, Volatility Loss, Phosphorous and Ball Rust Test. In the H&M test, the tested oil shall remain homogeneous and miscible when mixed with SAE reference oils. Table 15 discloses the results. According to ASTM D 4485-99b, the oil meets the bench test of the ILSAC GF-3/API SL minimum performance standard and passed all API-SL bench tests requirements.

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Table 15: Formula AA

Description of the Test	Test Method	Test Result	GF-3/API SL Limit
H&M (Homogeneity & Miscibility) Test	FTM-3470.1	non-separation	non-separation
TEOST MHT 4,	D 6335M	/	/
Total Deposit (Rod + Filter)		20.6 mg	45 mg (max)
Foam Test GF-3	D 892	/	/
Sequence I , foaming/setting		0/0	10 max./0
Sequence II , foaming/setting		5/0	50 max./0
Sequence III, foaming/setting		0/0	10 max./0
High Temperature Foam Test	D 6082	/	/
Foam Tendency		20	100 ml (max)
Foam Stability		0	0
EOFT (Engine Oil Filterability Test),	GM 9099P	/	/
% Flow Reduction		15.07	50 (max)
EOWTT (Engine Oil Filterability/Water Tolerance Test)	GM 9099P	/	/
with 0.6% water		22.12	50 (max)
with 1.0% water		12.17	50 (max)
with 2.0% water		13.9	50 (max)
with 3.0% water		15.63	50 (max)
Gelation Index	D 5133	8.3	12 (max)
NOACK, Volatility % wt loss	D 972	7.11	15 max
Volatility Loss at 371°F	D 6417	3.20%	10% max
Phosphorous, wt%	D 4951	0.093	0.1% max
Ball Rust Test, Average Gray Value	D 6557	134	100 min

The formulation AA was also submitted for ASTM Sequence IIIF engine tests.

The Sequence IIIF Test is a fired-engine, dynamometer lubricant test for evaluating automotive engine oils for certain high-temperature performance characteristics, including oil thickening, sludge and varnish deposition, oil consumption, and engine wear. The Sequence IIIF Test utilizes a 1996 model Buick 3800 Series II, water-cooled, 4-cycle, V-6 engine as the test apparatus. The Sequence IIIF test engine is an overhead valve design (OHV) and uses a single camshaft operating both intake and exhaust valves via pushrods and hydraulic valve lifters in a sliding-follower arrangement. The engine uses one intake and one exhaust valve per cylinder. Introduction is handled by a modified GM port fuel injection system setting the Air-to-Fuel ratio at 15:1. The test engine is overhauled prior to each test, during which critical engine dimensions are measured and rated or measured parts (pistons, camshaft, valve lifters, etc). The Sequence IIIF Test consists of a 10-minute operational check, followed by 80 hours of engine operation at moderately high speed, load, and temperature conditions. Following each 10-hour segment, and the 10-minute operational check, oil samples are drawn from the engine. The kinematic viscosities of the 10-hour segment samples are compared to the viscosity of the 10-minute sample to determine the viscosity increase of the test oil.

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The Sequence IIIF Test is operated at the test states in Table 16 during the 80 hour portion of the test. Table 17 discloses the results. According to ASTM Sequence IIIF engine tests, the oil meets the bench test of the ILSAC GF-3/API SL minimum performance standard and passed all API-SL bench tests requirements.

5

Table 16: Test states of Sequence IIIF testing

Parameter	Set Point
Engine Speed	3600 r/min
Engine Load	200 N-m
Oil Filter Block Temperature	155 °C
Coolant Outlet Temperature	122 °C
Fuel Pressure	365 kPa
Inlet Air Temperature	27 °C
Inlet Air Pressure	0.05 kPa
Inlet Air Dew Point	16.1 °C
Exhaust Back Pressure	6 kPa
Engine Coolant Flow	160 L/min
Breather Tube Coolant Flow	10 L/min
Engine Oil Cooler Flow	12 L/min
Air-to-Fuel Ratio	15.0 : 1
Breather Tube Coolant Outlet Temperature	40 °C

Table 17: Formula AA

Description of the Test	Test Result	GF-3/API SL Limit
Viscosity Increase (KV 40°C)	156.10 %	275 % max
Weighted Piston Skirt Vanish Rating	9.59	9.0 min
Weighted Piston Deposit Rating	6.19	4.0 min
Hot Struck Piston Rings	0	None Allowed
Cam plus Lifter Wear, Average, μm	16.7	20 max
Oil Consumption L	1.83	5.2 max
Number of Cold Struck Rings	0	N.R.
Average Oil Ring Plugging, %	0	N.R.

EXAMPLE 12

To reduce the cost of the lubricants, a less expensive dibase ester, Esterex A41, was used. Table 18 discloses a prototype formulation for an 5W-30 SAE grade. Other grades are also easy to formulate with the less expensive dibase ester. Other less expensive dibase esters include Esterex NP 451 and NP 471. Table 18 further shows the properties of the formulation.

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Table 18: Formulation and Physical Properties of Formulation AB

Formulation		AB
SAE Grade		5W-30
Components	Description	wt %
Lz 7764	VII	1.30
Lz 7075F	VII	1.3
Excel 575-HC	Group II Oil	25
Cargill AP560	Modified vegetable oil	40.30
Esterex A41	Dibase ester	20.0
Lubrizol 20000	DI	12.00
Viscoplex 1-3004	PPD	0.1
Total wt %		100.00%
Physical Properties		
Kin. Vis @ 100°C		10.5 cSt
@ 40°C		56.1cSt
VI		179
CCS -35°C		5210
CCS -30°C		10270
TBS@ 150°C		3.32
Brookfield Temp		
@ 30,000 cP		-30.3°C
@ 40,000 cP		-31.4°C
Gelation Index		8.1
Gelation Temp.		-32°C
MRV TP-1 @ -35°C		15000 cP
MRV YS @ -35°C		0
Pour Point		< -50°C
NOACK, wt% loss		8.6

As demonstrated above, embodiments of the invention provide an environmentally friendly lubricant that meets API SL bench test specifications, and is overall at least 60% biodegradable in ASTM D-5864-95 biodegradability testing.

- 5 Additional characteristics and advantages provided by embodiments of the invention are apparent to those skilled in the art.

While the invention has been described with respect to a limited number of embodiments, the specific features of one embodiment should not be attributed to other embodiments of the invention. No single embodiment is representative of all aspects of the inventions. In some embodiments, the compositions may include numerous compounds and/or characteristics not mentioned herein. In other embodiments, the compositions do not include, or are substantially free of, one or more compounds and/or characteristics not enumerated herein. Variations and modifications from the described embodiments exist. For example, the environmentally friendly lubricant need not be a mixture within the compositions given above. It can comprise any amount of components, so long as the properties desired in the environmentally friendly lubricant

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are met. It should be noted that the application of the environmentally friendly lubricant composition is not limited to lubricants for automobiles; it can be used in any environment which requires an environmentally friendly lubricant, such as a trucks, vans or buses. It is noted that the methods for making and using the environmentally friendly

5 lubricant composition are described with reference to a number of steps. These steps can be practiced in any sequence. One or more steps may be omitted or combined but still achieve substantially the same results. The appended claims intend to cover all such variations and modifications as falling within the scope of the invention.

What is claimed is:

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1. An environmentally friendly lubricant, comprising:
 - a) a transesterified triglycerol oil; and
 - b) a first ester different from the triglycerol oil;wherein the environmentally friendly lubricant is at least 60% biodegradable and has
5 a gelation index less than about 12.
2. A method of making an environmentally friendly lubricant, the method comprising:
blending a transesterified triglycerol oil and a first ester
wherein the environmentally friendly lubricant is at least 60% biodegradable and has
10 a gelation index less than about 12.
3. In claim 1 or 2, wherein the environmentally friendly lubricant further comprises:
 - c) a second ester as a polar viscosity index improver; and
 - d) a hydrogenated copolymer as a non-polar viscosity index improverwherein the second ester is different from the first ester and the triglycerol oil.
- 15 4. The environmentally friendly lubricant of claim 3 further comprising:
 - e) a dispersant/inhibitor package; and
 - f) at least one additive.
5. The environmentally friendly lubricant of claim 3 wherein the hydrogenated olefin copolymer is a hydrogenated ethylene-propene viscosity index improver.
- 20 6. In claim 1 or 2, wherein the transesterified triglycerol oil is in the amount from about 30 to about 85 wt%.
7. In claim 1 or 2, wherein the first ester is in the amount from about 10 to about 30 wt%.
8. The environmentally friendly lubricant of claim 3 wherein the second ester is in
25 the amount from about 0.1 to about 3 wt%.
9. The environmentally friendly lubricant of claim 3 wherein the hydrogenated olefin copolymer is in the amount from about 0.1 to about 6 wt%.
10. The environmentally friendly lubricant of claim 4 wherein the dispersant/inhibitor package is in the amount from about 8 to about 14 wt%.

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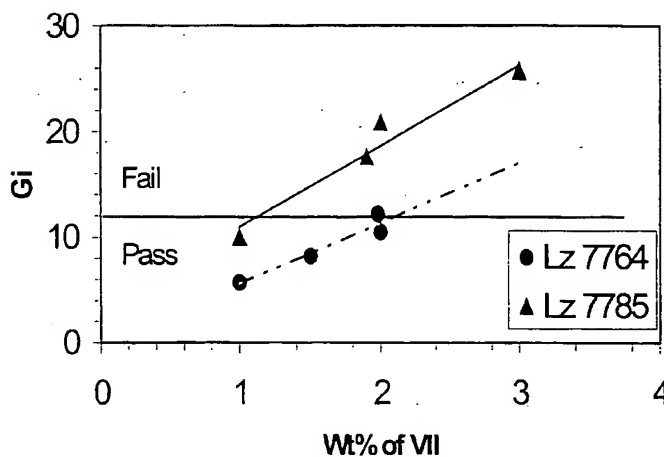
11. The environmentally friendly lubricant of claim 4 wherein the at least one additive is a pour point depressant, antioxidant, friction modifier, rust inhibitor, corrosion inhibitor anti-foaming agent or a combination thereof in the amount from about 0.1 to about 5 wt%.
- 5 12. The environmentally friendly lubricant of claim 3 further comprising mineral oil or synthetic oil.
13. The environmentally friendly lubricant of claim 12 wherein the mineral oil or synthetic oil is in the amount from about 0.1 to about 30 wt%.
- 10 14. In claim 1 or 2, wherein the transesterified triglycerol oil is a mixture of a glycerol polyol ester and a non-glycerol polyol ester.
15. In claim 1 or 2, wherein the transesterified triglycerol oil comprises a glycerol polyol ester but not a non-glycerol polyol ester.
16. In claim 1 or 2, wherein the transesterified triglycerol oil comprises a non-glycerol polyol ester but not a glycerol polyol ester.
- 15 17. In claim 1 or 2, wherein the transesterified triglycerol oil is obtained by transesterifying a vegetable oil with an ester of short-chain fatty acids.
18. In claim 1 or 2, wherein the transesterified triglycerol oil is obtained by transesterifying a vegetable oil with a polyol ester.
19. In claim 1 or 2, wherein the first ester is dibasic ester.
- 20 20. In claim 1 or 2, wherein the first ester is tribasic ester.
21. In claim 1 or 2, wherein the first ester is polyol ester.
22. In claim 1 or 2, wherein the environmentally friendly lubricant is an automobile engine oil.

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Figure 1



INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C10M101/04 C10M169/04 //(C10M169/04,101:04,101:02,105:36, 105:38,129:72,129:74,143:02,143:00,159:08),C10N30:00,C10N40:25, C10N60:00 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C10M Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 338 471 A (LAL KASTURI) 16 August 1994 (1994-08-16) column 1, line 7 - line 16 column 1, line 51 -column 2, line 2 column 3, line 60 -column 6, line 30 column 50, line 59 -column 52, line 25 column 53, line 16 - line 31 ---	1-22
A	US 5 399 275 A (LANGE RICHARD M ET AL) 21 March 1995 (1995-03-21) column 1, line 10 - line 18 column 1, line 65 -column 2, line 19 column 16, line 44 -column 18, line 2 ---	1-22
A	US 5 451 334 A (BONGARDT FRANK ET AL) 19 September 1995 (1995-09-19) column 2, line 16 -column 4, line 5 --- -/--	1-22
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
Date of the actual completion of the international search 4 December 2002		Date of mailing of the international search report 11/12/2002
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Rotsaert, L

INTERNATIONAL SEARCH REPORT

Inte Application No
PCT/US 02/30233

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 773 391 A (LAL KASTURI ET AL) 30 June 1998 (1998-06-30) column 34, line 15 -column 35, line 39; tables III-VI ---	1-22
A	EP 0 843 000 A (FUJI OIL CO LTD) 20 May 1998 (1998-05-20) the whole document ---	1-22
A	US 6 278 006 B1 (KODALI DHARMA R ET AL) 21 August 2001 (2001-08-21) cited in the application column 2, line 7 -column 3, line 5 column 7, line 54 -column 8, line 64 -----	1-22

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Application No

PCT/US 02/30233

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5338471	A	16-08-1994	AU 673104 B2	24-10-1996
			AU 7446694 A	04-05-1995
			CA 2117957 A1	16-04-1995
			EP 0651044 A2	03-05-1995
			JP 7157790 A	20-06-1995
US 5399275	A	21-03-1995	AU 672248 B2	26-09-1996
			AU 5246193 A	30-06-1994
			CA 2111776 A1	19-06-1994
			DE 69328072 D1	20-04-2000
			DE 69328072 T2	02-11-2000
			EP 0602981 A1	22-06-1994
			ES 2145037 T3	01-07-2000
			JP 6240283 A	30-08-1994
			ZA 9309327 A	25-08-1994
US 5451334	A	19-09-1995	DE 3927155 A1	21-02-1991
			BR 9007600 A	30-06-1992
			CA 2065011 A1	18-02-1991
			DE 59003632 D1	05-01-1994
			WO 9102784 A1	07-03-1991
			EP 0486575 A1	27-05-1992
			ES 2060193 T3	16-11-1994
			JP 5503949 T	24-06-1993
US 5773391	A	30-06-1998	AU 697824 B2	15-10-1998
			AU 3778095 A	23-05-1996
			BR 9504838 A	07-10-1997
			CA 2162441 A1	16-05-1996
			DE 69510755 D1	19-08-1999
			DE 69510755 T2	02-03-2000
			EP 0712834 A1	22-05-1996
			ES 2136805 T3	01-12-1999
			JP 8208563 A	13-08-1996
			SG 49568 A1	15-06-1998
EP 0843000	A	20-05-1998	DE 69716380 D1	21-11-2002
			EP 0843000 A1	20-05-1998
			US 6117827 A	12-09-2000
			WO 9746641 A1	11-12-1997
			JP 10053780 A	24-02-1998
US 6278006	B1	21-08-2001	AU 3210600 A	01-08-2000
			BR 0008177 A	06-11-2001
			EP 1144563 A2	17-10-2001
			JP 2002534561 T	15-10-2002
			NO 20013561 A	18-09-2001
			WO 0041515 A2	20-07-2000
			US 6465401 B1	15-10-2002